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PATENT
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IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: Terunori FUJITA et al. Conf.: 9790
Appl. No.: 09/942,706 Group: 1755
Filed: August 31, 2001 Examiner: J. Pasterczyk
For: OLEFIN POLYMERIZATION CATALYSTS, TRANSITION METAL COMPOUNDS, PROCESSES FOR OLEFIN POLYMERIZATION, AND ALPHA-OLEFIN/CONJUGATED DIENE COPOLYMERS

L E T T E R

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

January 13, 2004

Sir:

Subsequent to the filing of the above-identified application on August 31, 2001, attached hereto are English translations of Japanese Priority Documents 9-109922 filed April 25, 1997 and 10-50541 filed March 3, 1998, that should be made of record in the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By


Marc S. Weiner, #32,181
P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

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Attachment(s)



DECLARATION

I, Shigeru FUCHITA, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a full, true and faithful translation made by me of Japanese Application for Patent No. 9-109922.

I make this solemn declaration conscientiously believing the same to be true.

November 11, 2002



Shigeru FUCHITA

[Document] Application for Patent

[Reference No.] Y09620-010

[Filing Date] April 25, 1997

[To:] Director-General of the Patent Office

[Title of the invention]

Olefin polymerization catalysts and processes for olefin polymerization

[Number of Claims] 2

[Inventor(s)]

Address: c/o Mitsui Petrochemicals, Inc.,
1-2, Waki 6-chome, Waki-cho, Kuga-gun,
Yamaguchi, Japan

Name: Yasushi TOHI

Address: c/o Mitsui Petrochemicals, Inc.,
1-2, Waki 6-chome, Waki-cho, Kuga-gun,
Yamaguchi, Japan

Name: Haruyuki MAKIO

Address: c/o Mitsui Petrochemicals, Inc.,
1-2, Waki 6-chome, Waki-cho, Kuga-gun,
Yamaguchi, Japan

Name: Terunori FUJITA

[Applicant(s)]

Reference No.: 000005887

Name: Mitsui Petrochemicals, Inc.

[Agent]

Reference No.: 100081994

Patent Attorney:

Name: Shunichiro SUZUKI

[Indication of Fee]

Deposit Account No.: 014535

Amount: 21000

[List of the Appended Documents]

Description	1
Drawing	1
Abstract	1
General Power of Attorney No.:	9106935

[Necessity or not of group] Necessity

[Document] Specification

[Title of the invention]

Olefin polymerization catalysts and processes for olefin polymerization

5 [What is claimed is:]

1. An olefin polymerization catalyst comprising:

(A) a transition metal compound represented by the following formula (I), and

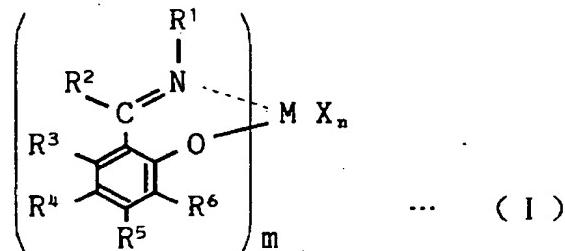
(B) at least one compound selected from:

10 (B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound (A) to form an ion pair:

15



wherein M is a transition metal atom of Group 3 to Group 11
20 of the periodic table,

m is an integer of 1 to 3,

R¹ to R⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an alkoxy group, an

aryloxy group, an ester group, an amido group, an amino group, a sulfonamido group, a nitrile group or a nitro group, and two or more of them may be bonded to each other to form a ring, when m is 2 or more, two of the groups R¹ to R⁶ may be bonded

5 to each other,

n is a number satisfying a valence of M, and

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a 10 sulfur-containing group or a silicon-containing group, and when n is 2 or more, plural groups X may be the same or different and may be bonded to each other to form a ring.

2. A process for olefin polymerization, comprising
15 polymerizing or copolymerizing an olefin in the presence of the olefin polymerization catalyst as claimed in claims 1.

[Detailed description of the invention]

[0001]

20 [Field of the invention]

The present invention relates to novel olefin polymerization catalysts and processes for olefin polymerization using the olefin polymerization catalysts.

[0002]

[Background of the invention]

As olefin polymerization catalysts, so-called "Kaminsky catalysts" are well known. The Kaminsky catalysts have extremely high polymerization activities, and by the use of them, polymers of narrow molecular weight distribution can be obtained. As the transition metal compounds used for the Kaminsky catalysts, for example,

bis(cyclopentadienyl)zirconium dichloride (see: Japanese Patent Laid-Open Publication No. 19309/1983) and ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride (see: Japanese Patent Laid-Open Publication No. 130314/1986) are known. It is also known that the olefin polymerization activities or the properties of the resulting polyolefins greatly vary when different transition metal compounds are used in the polymerization. Further, transition metal compounds having a ligand of diimine structure have been recently proposed as novel olefin polymerization catalysts (see: International Patent Publication No. 9623010).

[0003]

Polyolefins generally have excellent mechanical properties, and therefore they are used in various fields such as molded products of all sorts. However, with variation of requirements for the polyolefins, polyolefins of various properties have been desired in recent years. Moreover,

increase of productivity has been also desired.

[0004]

Under such circumstances, there has been desired development of olefin polymerization catalysts having 5 excellent olefin polymerization activities and capable of producing polyolefins of excellent properties.

[0005]

[Object of the invention]

It is an object of the present invention to provide an 10 olefin polymerization catalyst having excellent olefin polymerization activities and a process for olefin polymerization using the olefin polymerization catalyst.

[0006]

[Summary of the invention]

15 The olefin polymerization catalyst according to the present invention comprises:

(A) a transition metal compound represented by the following formula (I), and

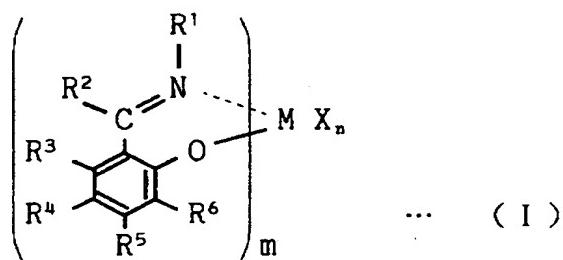
(B) at least one compound selected from:

20 (B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition metal compound to form an ion pair:

[0007]



5

[0008]

wherein M is a transition metal atom of Group 3 to Group 11 of the periodic table,

m is an integer of 1 to 3,

10 R¹ to R⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an alkoxy group, an aryloxy group, an ester group, an amido group, an amino group, a sulfonamido group, a nitrile group or a nitro group, and two
15 or more of them may be bonded to each other to form a ring, when m is 2 or more, two of the groups R¹ to R⁶ may be bonded to each other,

n is a number satisfying a valence of M, and

20 X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group or a silicon-containing group, and when n is 2 or more, plural groups X may be the same or different and may be bonded to each other to form a ring.

The process for olefin polymerization according to the present invention comprises polymerizing or copolymerizing an olefin in the presence of the above-mentioned olefin polymerization catalyst.

5 [0009]

[Specific description of the invention]

The olefin polymerization catalyst of the present invention and the process for olefin polymerization using the catalyst are described specifically hereinafter.

10 [0010]

The meaning of the term "polymerization" used herein is not limited to "homopolymerization" but may comprehend "copolymerization". Also, the meaning of the term "polymer" used herein is not limited to "homopolymer" but may comprehend 15 "copolymer".

[0011]

The olefin polymerization catalyst of the invention is formed from:

(A) a transition metal compound represented by the 20 following formula (I), and

(B) at least one compound selected from:

(B-1) an organometallic compound,

(B-2) an organoaluminum oxy-compound, and

(B-3) a compound which reacts with the transition

metal compound to form an ion pair.

[0012]

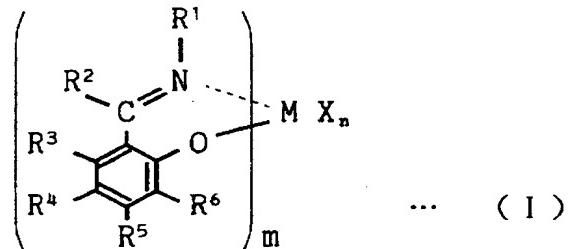
First, the catalyst components for forming the olefin polymerization catalyst of the invention are described.

5 (A) Transition metal compound

The transition metal compound (A) for use in the invention is a compound represented by the following formula (I).

[0013]

10



[0014]

15

In the above formula, M is a transition metal atom of Group 3 to Group 11 of the periodic table, preferably Groups 4 or 9, especially preferably titanium, zirconium, hafnium, iron, cobalt, copper or rhodium.

[0015]

20

m is an integer of 1 to 3.

R¹ to R⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an alkoxy group, an aryloxy group, an ester group, an amido group, an amino group,

a sulfonamido group, a nitrile group or a nitro group.

[0016]

The halogen atom is fluorine, chlorine, bromine or iodine.

Examples of the hydrocarbon groups include

5 straight-chain or branched alkyl groups of 1 to 20, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl and hexyl; aryl groups of 6 to 20, such as phenyl and naphthyl; substituted aryl group wherein the aryl groups are substituted with 1 to 5 substituent groups,
10 such as alkyl groups of 1 to 20 carbon atoms, aryl groups of 6 to 20 carbon atoms, alkoxy groups, aryloxy groups or the like.

[0017]

Examples of the hydrocarbon-substituted silyl groups include methylsilyl, dimethylsilyl, trimethylsilyl,
15 ethylsilyl, diethylsilyl, triethylsilyl, diphenylmethylsilyl.

[0018]

Examples of the alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and tert-butoxy.

Examples of the aryloxy groups include phenoxy,
20 2,6-dimethylphenoxy and 2,4,6-trimethylphenoxy.

[0019]

Examples of the ester groups include acetyloxy, benzyloxy, methoxycarbonyl, phenoxy carbonyl and p-chlorophenoxy carbonyl.

[0020]

Examples of the amido groups include acetamido, N-methylacetamido and N-methylbenzamido.

Examples of the amino groups include dimethylamino, ethylmethylamino and diphenylamino.

5 [0021]

Examples of the sulfonamido groups include phenylsulfonamido, N-methylsulfonamido and N-methyl-p-toluenesulfonamido.

Two or more of the groups R¹ to R⁶, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, 10 an aromatic ring or a hydrocarbon ring containing a hetero atom such as a nitrogen atom.

[0022]

When m is 2 or more, two of the groups R¹ to R⁶ may be bonded to each other.

15 n is a number satisfying a valence of M, specifically an integer of 1 to 3.

[0023]

X is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 20 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group or a silicon-containing group, and when n is 2 or more, each X may be the same or different.

[0024]

Examples of the halogen atom include fluorine, chlorine,

bromine and iodine.

Examples of the hydrocarbon groups of 1 to 20 carbon atoms include alkyl groups, cycloalkyl groups, alkenyl groups, arylalkyl groups and aryl groups. Specifically, there can be 5 mentioned alkyl groups, such as methyl, ethyl, propyl, butyl, hexyl, octyl, nonyl, dodecyl and eicosyl; cycloalkyl groups, such as cyclopentyl, cyclohexyl, norbornyl and adamantyl; alkenyl groups, such as vinyl, propenyl and cyclohexenyl; arylalkyl groups, such as benzyl, phenylethyl and 10 phenylpropyl; and aryl groups, such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthryl and phenanthryl.

[0025]

The hydrocarbon groups of 1 to 20 carbon atoms include 15 halogenated hydrocarbon groups wherein the hydrocarbon groups of 1 to 20 carbon atoms may be substituted with halogen atoms.

Examples of the oxygen-containing groups include hydroxyl groups; alkoxy groups, such as methoxy, ethoxy, propoxy and butoxy; aryloxy groups, such as phenoxy, 20 methylphenoxy, dimethylphenoxy and naphthoxy; and arylalkoxy groups, such as phenylmethoxy and phenylethoxy.

[0026]

Examples of the sulfur-containing groups include groups wherein an oxygen atom of the oxygen-containing groups is

substituted with a sulfur atom; sulfonato groups, such as methylsulfonato, trifluoromethanesulfonato, phenylsulfonato, benzylsulfonato, p-toluenesulfonato, trimethylbenzenesulfonato, triisobutylbenzenesulfonato, p-chlorobenzenesulfonato and 5 pentafluorobenzenesulfonato; sulfinato groups, such as methylsulfinato, phenylsulfinato, benzylsulfinato, p-toluenesulfinato, trimethylbenzenesulfinato and pentafluorobenzenesulfinato.

[0027]

Examples of the silicon-containing groups include 10 monohydrocarbon-substituted silyl groups, such as methylsilyl and phenylsilyl; dihydrocarbon-substituted silyl groups, such as dimethylsilyl and diphenylsilyl; trihydrocarbon-substituted silyl groups, such as trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, dimethylphenylsilyl, 15 methyldiphenylsilyl, tritolylsilyl and trinaphthylsilyl; hydrocarbon-substituted silylether groups, such as trimethylsilylether; silicon-substituted alkyl groups, such as trimethylsilylmethyl; and silicon-substituted aryl groups, such as trimethylsilylphenyl.

20 [0028]

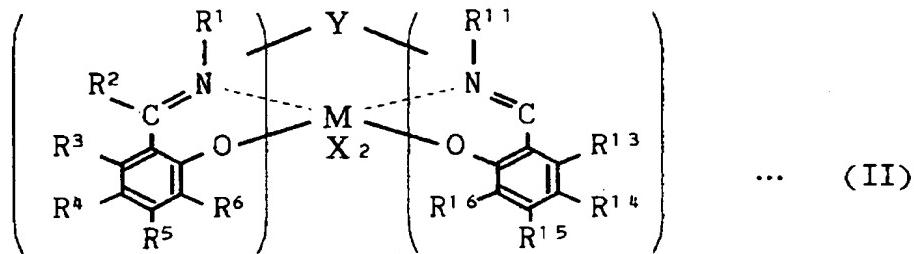
Of these, preferable are hydrocarbon groups of 1 to 20 halogen atoms or carbon atoms, or sulfonato groups.

When n is 2 or more, groups X may be bonded to each other to form a ring.

[0029]

In the transition metal compounds represented by the formula (I), the compound wherein m is 2 and two of the groups R¹ to R⁶ are bonded to each other is, for example, a compound 5 represented by the following formula (II).

[0030]



[0031]

In the above formula, M, R¹ to R⁶, and X are identical 15 with M, R¹ to R⁶, and X in the formula (I).

R¹¹ to R¹⁶ may be the same or different, and are each a hydrogen atom, a halogen atom, a hydrocarbon group, a hydrocarbon-substituted silyl group, an alkoxy group, an aryloxy group, an ester group, an amido group, an amino group, 20 a sulfonamido group, a nitrile group or a nitro group, specifically, the same atom or group as described for R¹ to R⁶. Two or more of these groups, preferably adjacent groups, may be bonded to each other to form an aliphatic ring, an aromatic ring or a hydrocarbon ring containing a hetero atom

such as a nitrogen atom.

[0032]

Y is a bonding group or a single bond for bonding at least one group selected from R¹ to R⁶ to at least one group selected 5 from R¹¹ to R¹⁶ (except a case of bonding R¹ and R¹¹ to each other).

[0033]

The bonding group Y is a group containing at least one element selected from among oxygen, sulfur, carbon, nitrogen, 10 phosphorus, silicon, selenium, tin, boron and the like. Examples of such groups include chalcogen atom-containing groups such as -O-, -S- and -Se-; nitrogen- or phosphorus-containing groups, such as -NH-, -N(CH₃)₂- , -PH- and -P(CH₃)₂-; hydrocarbon groups of 1 to 20 carbon atoms, such as -CH₂-, 15 -CH₂-CH₂- and -C(CH₃)₂-; residues of cyclic hydrocarbons of 6 to 20 carbon atoms, such as benzene, naphthalene and anthracene; residues of heterocyclic compounds having 3 to 20 carbon atoms and containing hetero atoms, such as pyridine, 20 quinoline, thiophene and furan; silicon atom-containing groups, such as -SiH₂- and -Si(CH₃)₂-; tin atom-containing groups, such as -SnH₂- and -Sn(CH₃)₂-; and boron atom-containing groups, such as -BH-, -B(CH₃)- and -BF-.

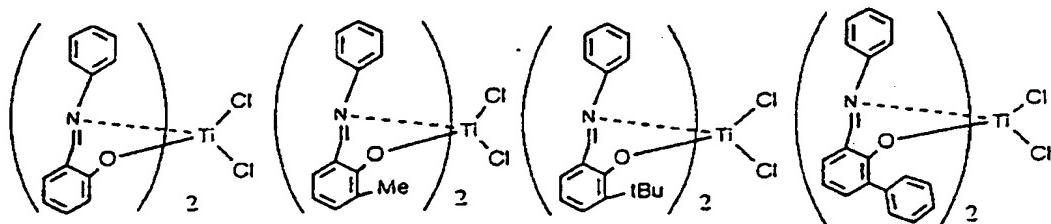
[0034]

Examples of the transition metal compounds represented

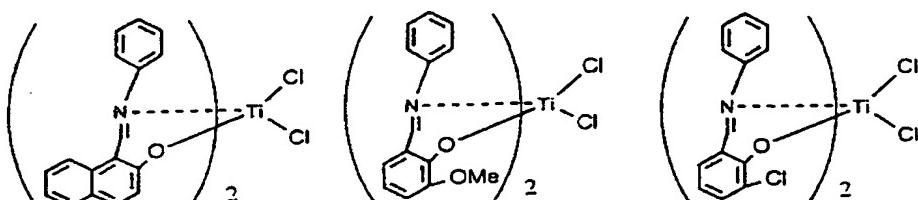
by the formula (I) are given below, but are not limited thereto.

[0035]

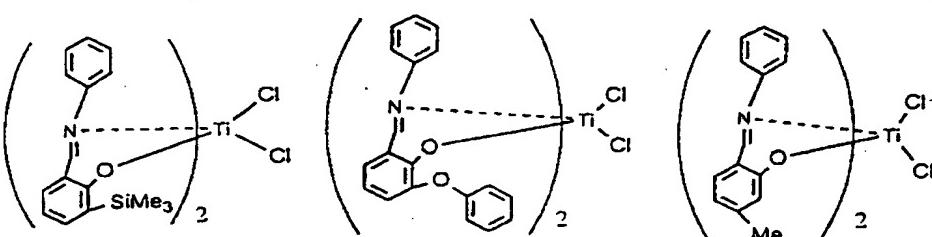
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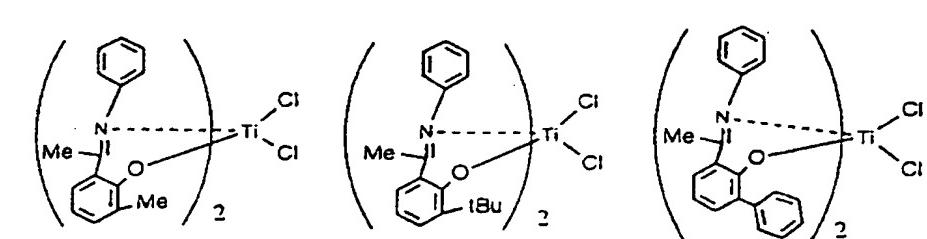
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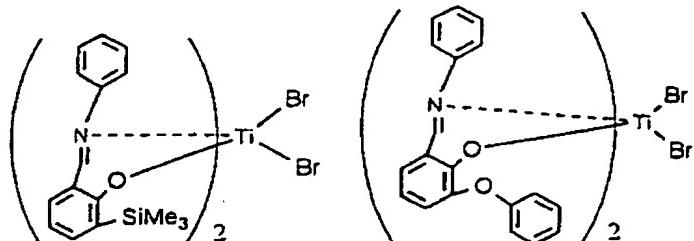
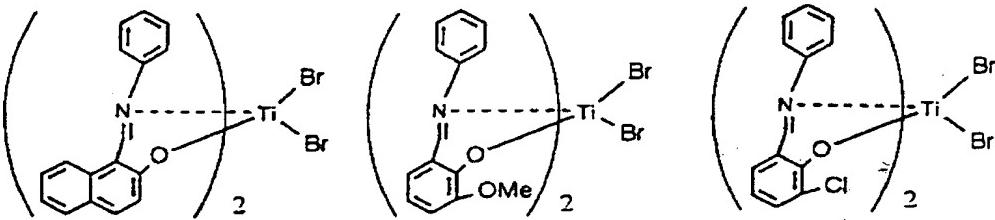
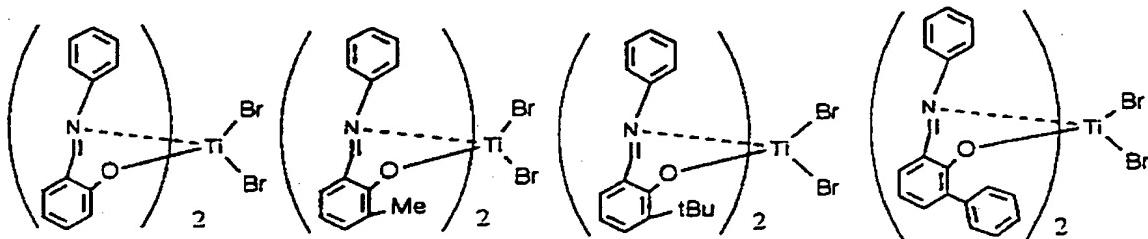
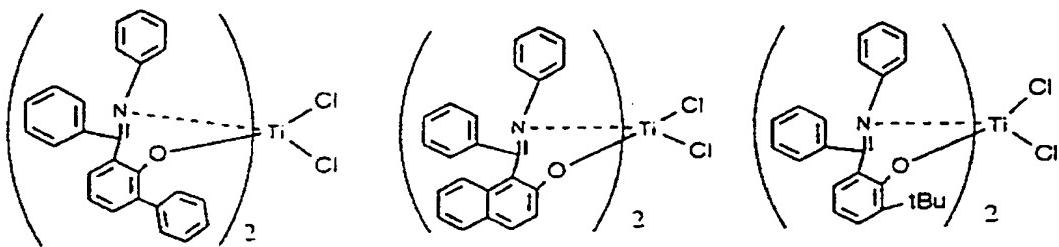
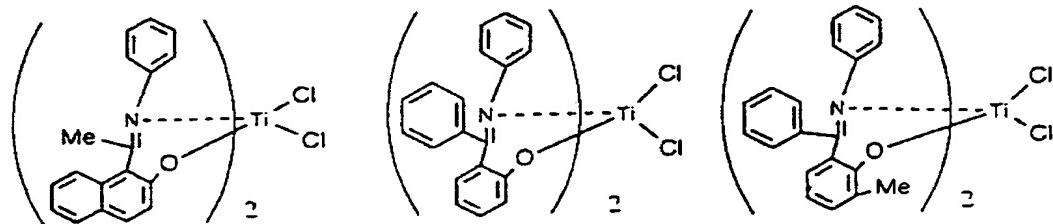
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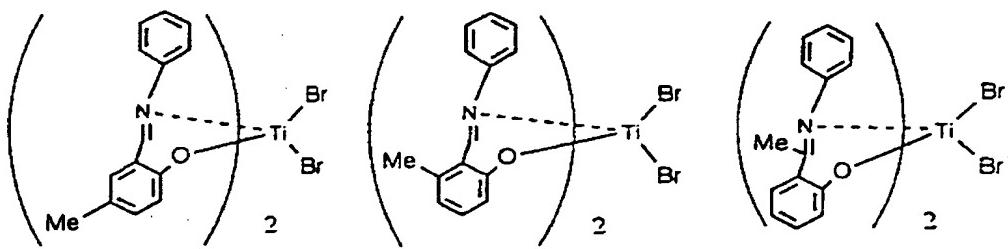
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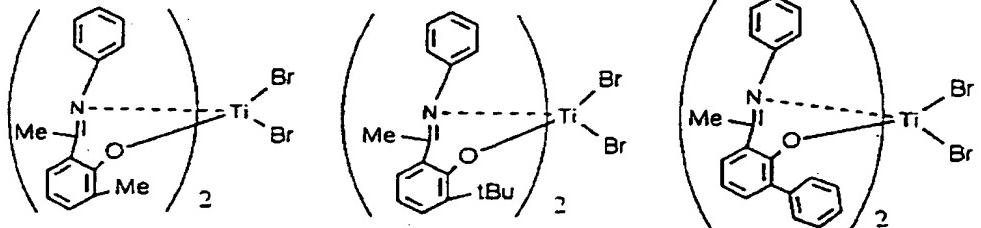
[0036]



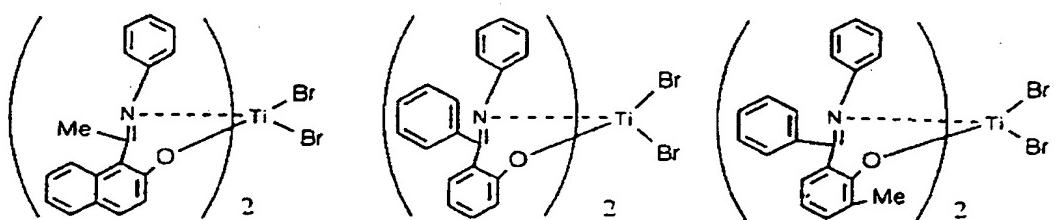
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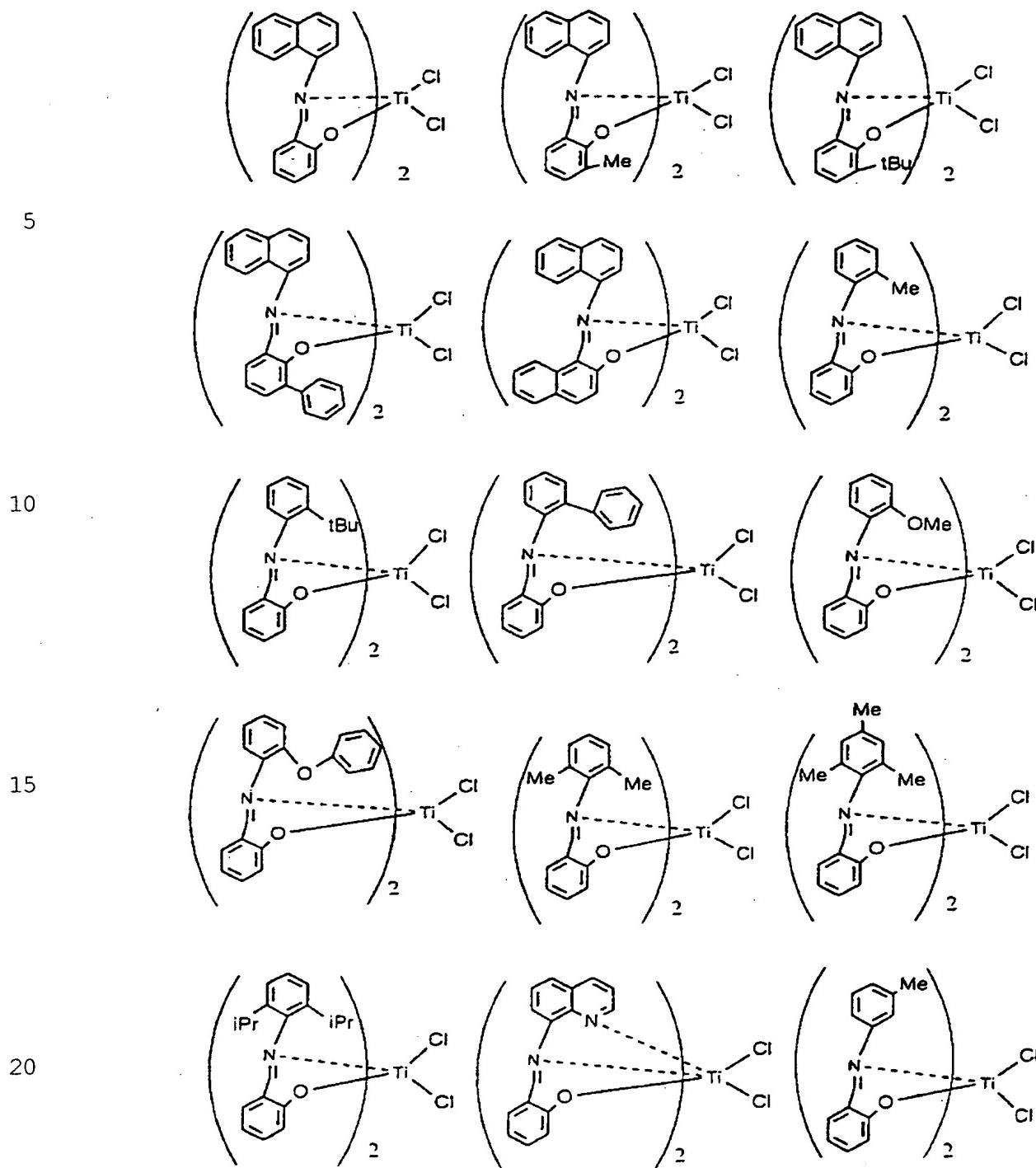


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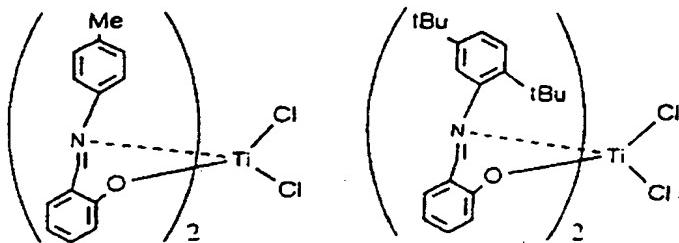
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[0038]

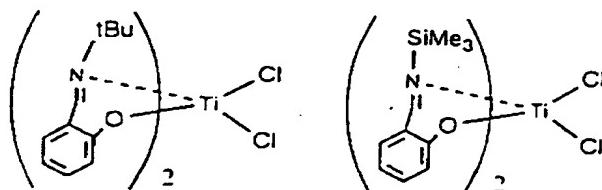


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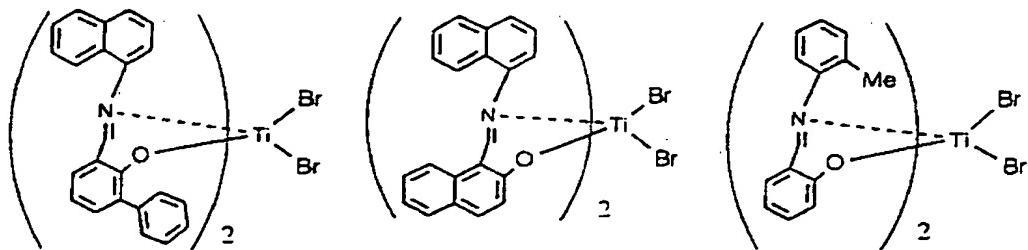
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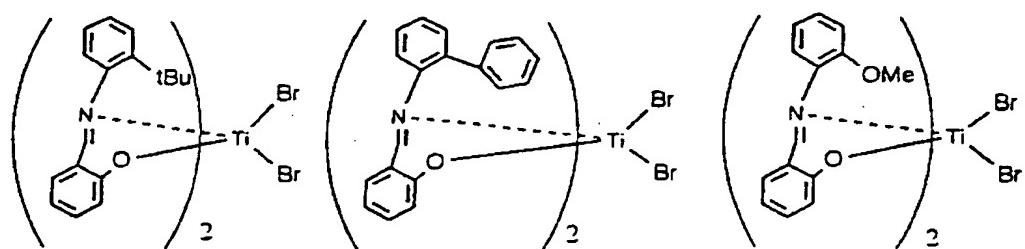
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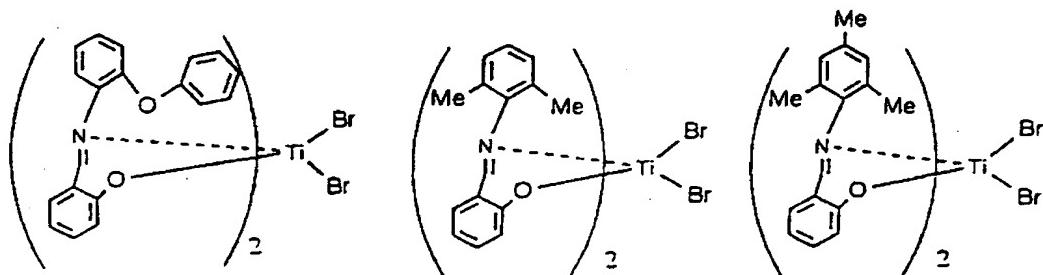


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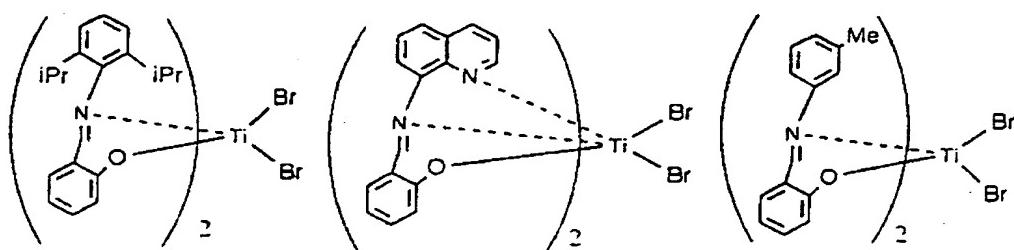


[0040]

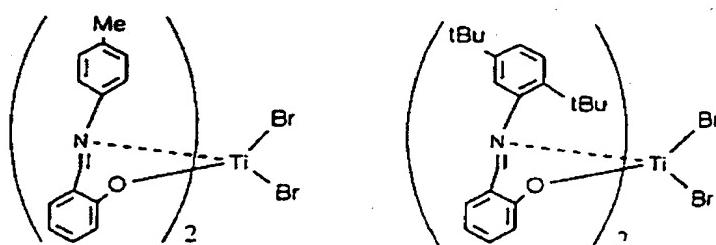
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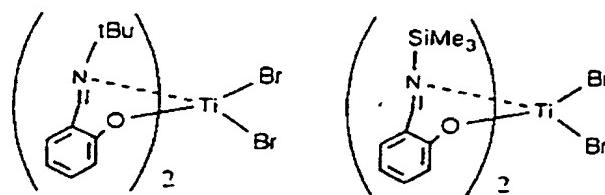
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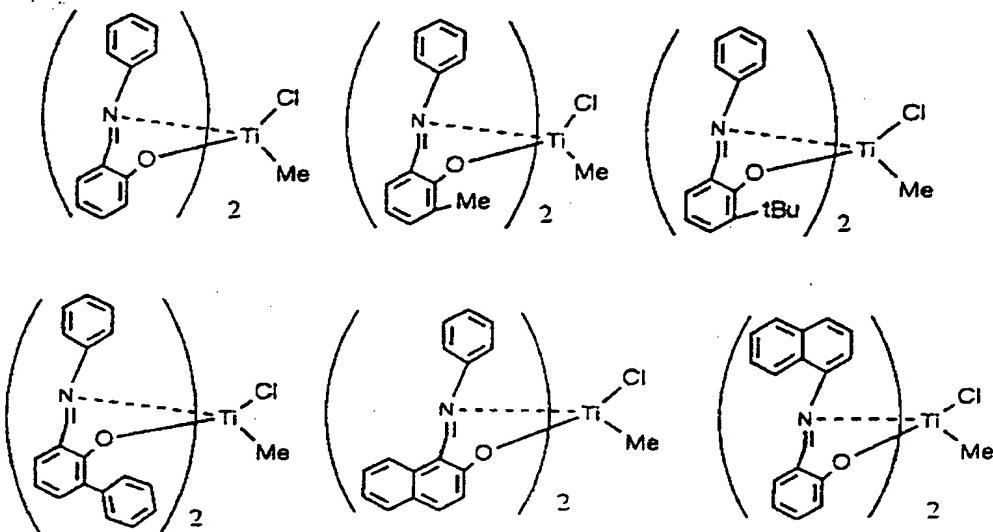


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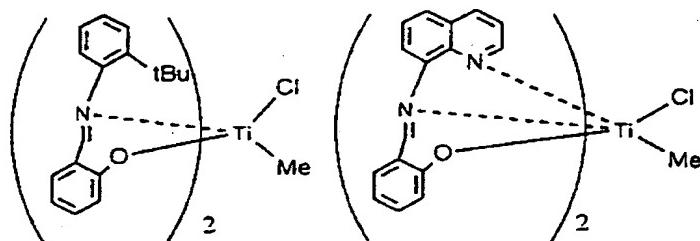


[0041]

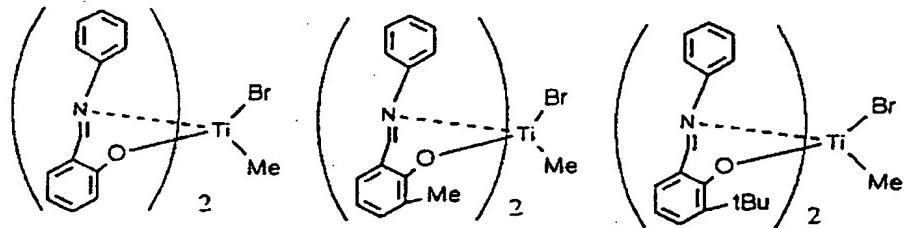
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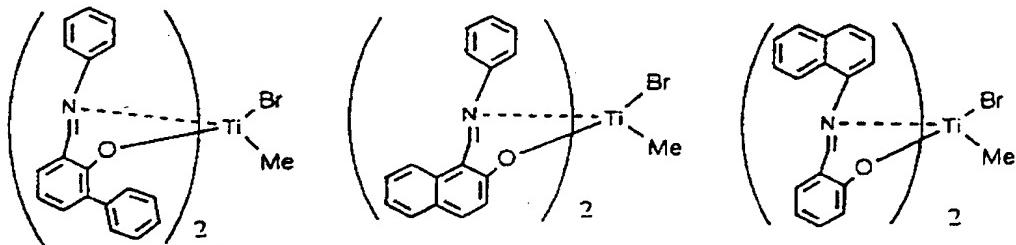
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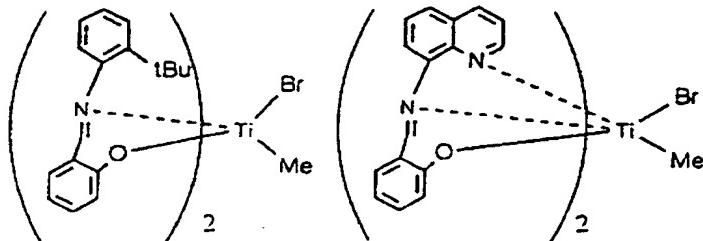
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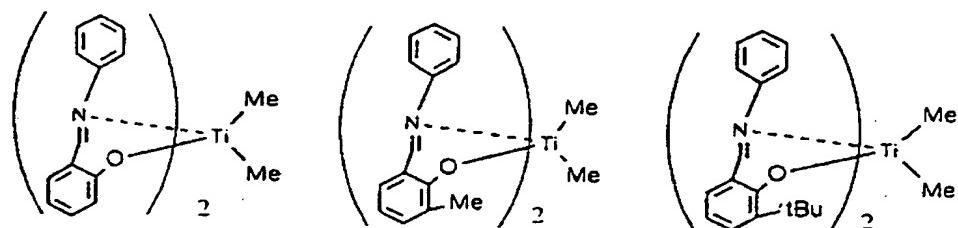
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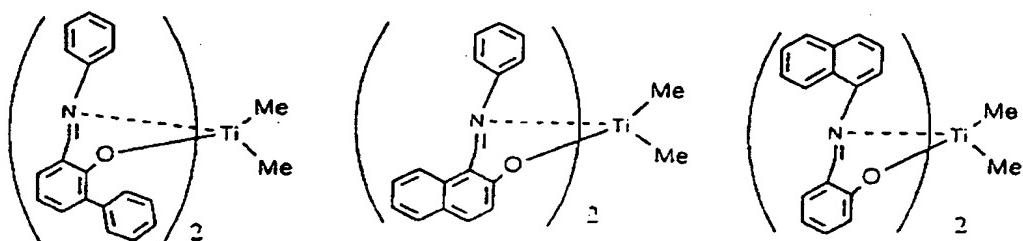
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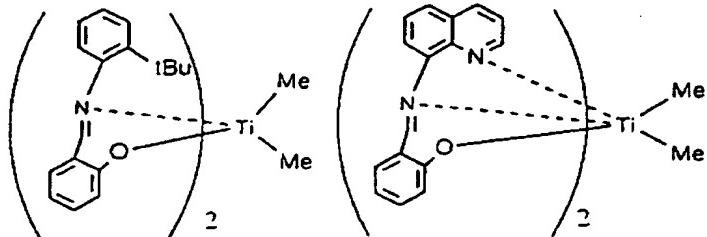
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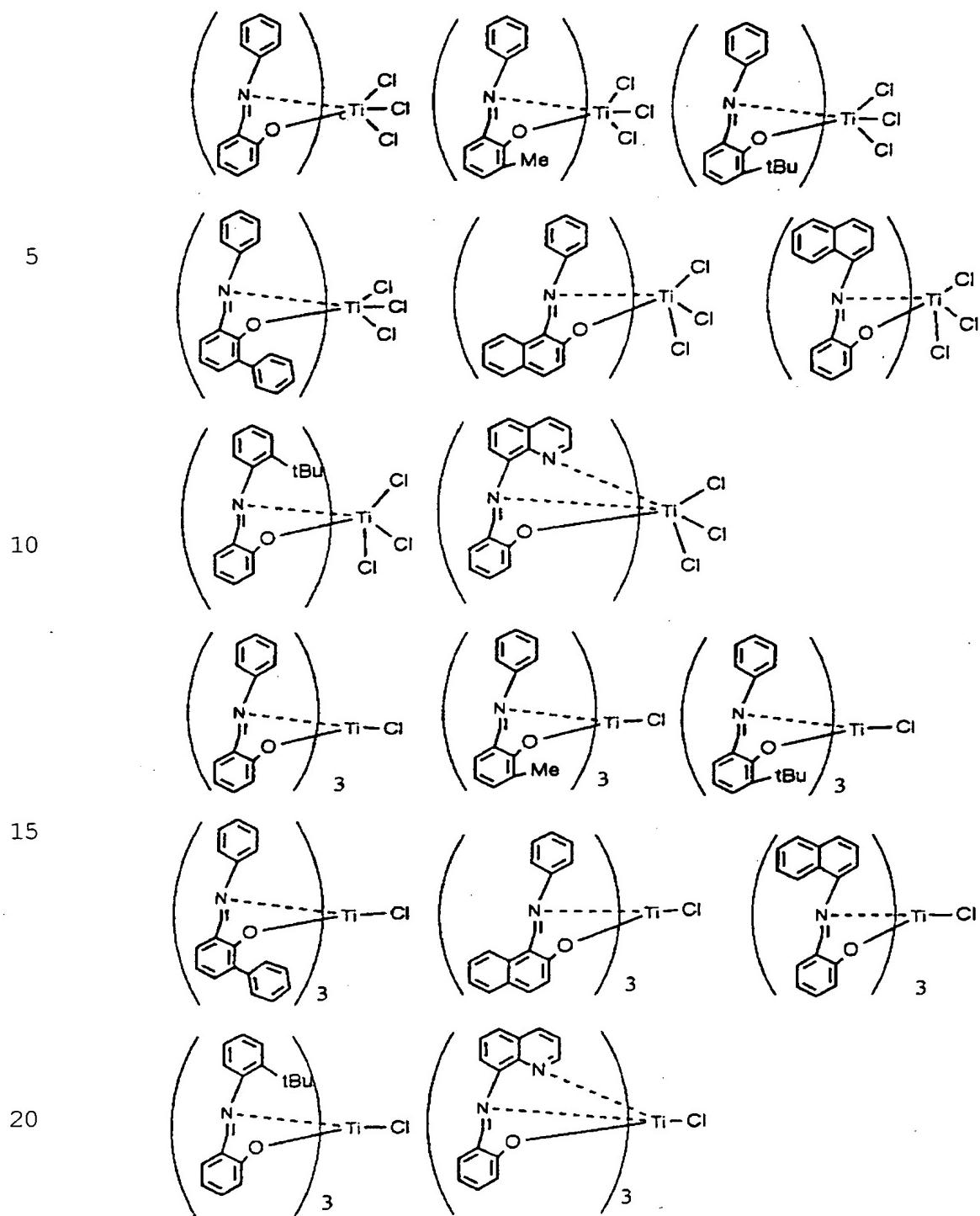
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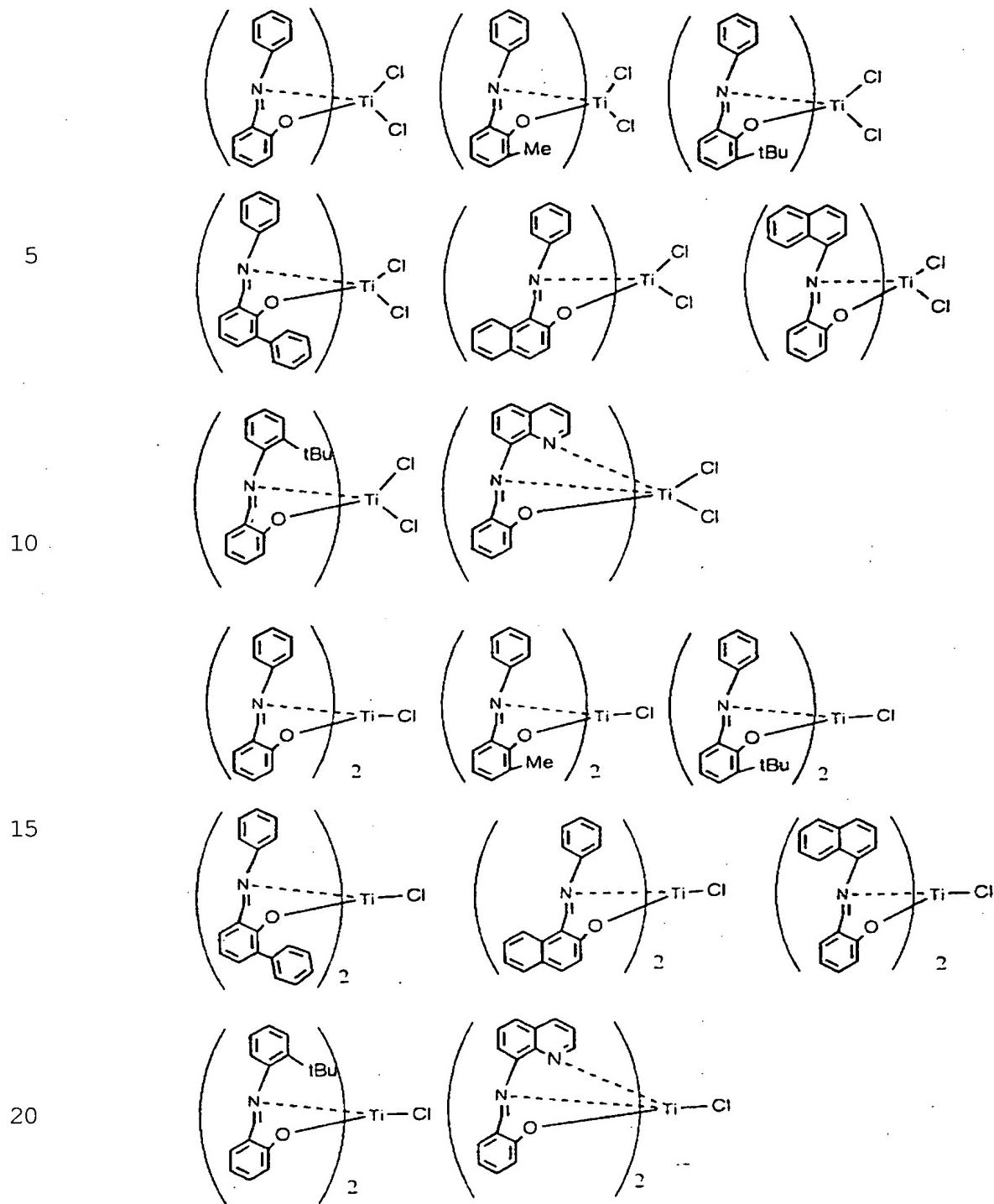


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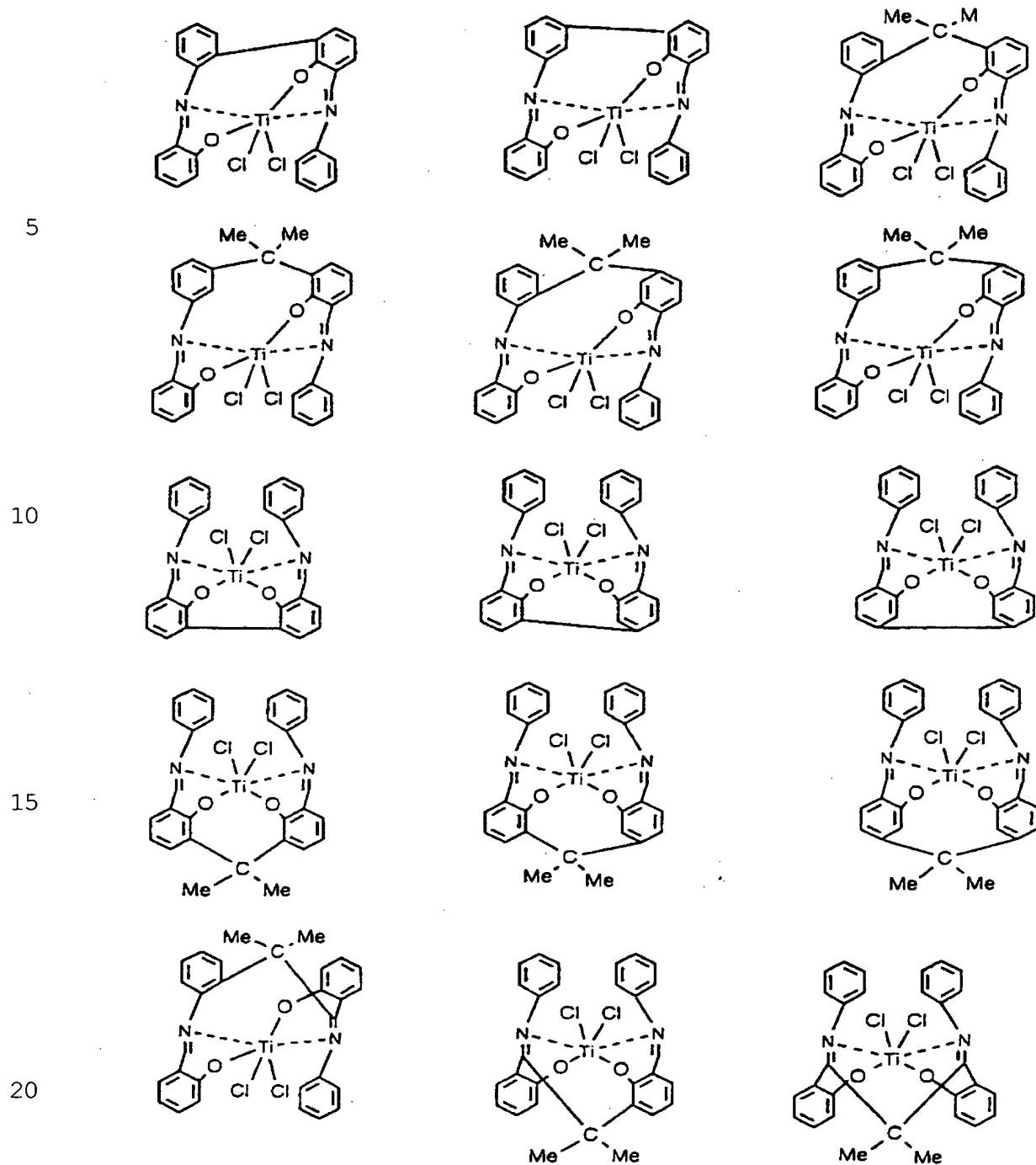


[0043]





[0045]



[0046]

In the above exemplification, Me is methyl, iPr is

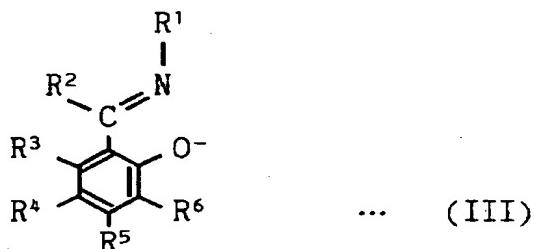
isopropyl and tBu is tert-butyl.

In the present invention, transition metal compounds wherein titanium is replaced with a metal such as zirconium, hafnium, iron, cobalt, copper or rhodium in the above-
5 exemplified compounds are also employable.

[0047]

Of the transition metal compounds, in compounds represented by the following formula (III) constituting the transition metal compounds:

10 [0048]



15

[0049]

wherein R¹ to R⁶ are identical with R¹ to R⁶ in the formula (I), an energy difference between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)
20 calculated by the Hamiltonian PM3 method of MOPAC VERSION 6.00 is preferably 8.50 or less, more preferably 8.00 or less.

[0050]

(B-1) Organometallic compound

As the organometallic compound (B-1), the below-described

organometallic compounds of metals of Group 1, Group 2, Group 12 and Group 13 of the periodic table are employable in the invention.

[0051]

(B-1a) Organoaluminum compound represented by the
5 following formula:



wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; X is a halogen atom;
10 and m , n , p and q are numbers satisfying the conditions of $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$, $0 \leq q < 3$ and $m+n+p+q = 3$.

[0052]

(B-1b) Alkyl complex compound of Group 1 metal and aluminum, that is represented by the following formula:



wherein M^2 is Li, Na or K; and R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms.

[0053]

20 (B-1c) Dialkyl compound of Group 2 metal or Group 12 metal, that is represented by the following formula:



wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a

hydrocarbon group of 1 to 4 carbon atoms; and M³ is Mg, Zn or Cd.

[0054]

Examples of the organoaluminum compounds (B-1a) include the following compounds.

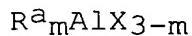
5 Organoaluminum compound represented by the following formula:



wherein R^a and R^b may be the same or different, and are each a hydrocarbon group of 1 to 15 carbon atoms, preferably a

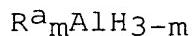
10 hydrocarbon group of 1 to 4 carbon atoms; and m is preferably a number satisfying the condition of 1.5≤m≤3.

Organoaluminum compound represented by the following formula:



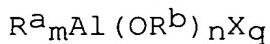
15 wherein R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; X is a halogen atom; and m is preferably a number satisfying the condition of 0<m<3.

Organoaluminum compound represented by the following
20 formula:



wherein R^a is a hydrocarbon group of 1 to 15 carbon atoms, preferably a hydrocarbon group of 1 to 4 carbon atoms; and m is preferably a number satisfying the condition of 2≤m<3.

Organooaluminum compound represented by the following formula:



wherein R^a and R^b may be the same or different, and are each
5 a hydrocarbon group of 1 to 15 carbon atoms, preferably a
hydrocarbon group of 1 to 4 carbon atoms; X is a halogen atom;
and m, n and q are numbers satisfying the conditions of $0 < m \leq 3$,
 $0 \leq n < 3$, $0 \leq q < 3$ and $m+n+q = 3$.

[0055]

10 Particular examples of the organooaluminum compounds
(B-1a) include:

tri-n-alkylaluminums, such as trimethylaluminum,
triethylaluminum, tri-n-butylaluminum, tripropylaluminum,
tripentylaluminum, trihexylaluminum, trioctylaluminum and
15 tridecylaluminum;

branched-chain trialkylaluminums, such as
triisopropylaluminum, triisobutylaluminum,
tri-sec-butylaluminum, tri-tert-butylaluminum,
tri-2-methylbutylaluminum, tri-3-methylbutylaluminum,
20 tri-2-methylpentylaluminum, tri-3-methylpentylaluminum,
tri-4-methylpentylaluminum, tri-2-methylhexylaluminum,
tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum;
tricycloalkylaluminums, such as tricyclohexylaluminum
and tricyclooctylaluminum;

triarylaluminums, such as triphenylaluminum and tritylaluminum;

dialkylaluminum hydrides, such as diisobutylaluminum hydride and diisobutylaluminum hydride;

5 trialkenylaluminums, such as triisoprenylaluminum represented by the formula $(i-C_4H_9)_xAl_y(C_5H_{10})_z$ (wherein x, y and z are positive numbers, and $z \geq 2x$);

alkylaluminum alkoxides, such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide;

10 dialkylaluminum alkoxides, such as dimethylaluminum methoxide, diethylaluminum ethoxide and dibutylaluminum butoxide;

alkylaluminum sesquialkoxides, such as ethylaluminum sesquiethoxide and butylaluminum sesquibutoxide;

partially alkoxyated alkylaluminums having an average
15 composition represented by $R^a_2.5Al(OR^b)0.5$;

dialkylaluminum aryloxides, such as diethylaluminum phenoxide, diethylaluminum(2,6-di-t-butyl-4-methylphenoxyde), ethylaluminumbis(2,6-di-t-butyl-4-methylphenoxyde), diisobutylaluminum(2,6-di-t-butyl-4-methylphenoxyde) and
20 isobutylaluminumbis(2,6-di-t-butyl-4-methylphenoxyde);

dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, dibutylaluminum chloride, diethylaluminum bromide and diisobutylaluminum chloride;

alkylaluminum sesquihalides, such as ethylaluminum

sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide;

partially halogenated alkylaluminums, such as ethylaluminum dichloride, propylaluminum dichloride and
5 butylaluminum dibromide;

dialkylaluminum hydrides, such as diethylaluminum hydride and dibutylaluminum hydride;

partially hydrogenated alkylaluminums, e.g., alkylaluminum dihydrides, such as ethylaluminum dihydride and
10 propylaluminum dihydride; and

partially alkoxylated and halogenated alkylaluminums, such as ethylaluminum ethoxychloride, butylaluminum butoxychloride and ethylaluminum ethoxybromide.

[0056]

15 Also employable are compounds analogous to the organoaluminum compound (B-1a). For example, there can be mentioned organoaluminum compounds wherein two or more aluminum compounds are combined through a nitrogen atom, such as $(C_2H_5)_2AlN(C_2H_5)Al(C_2H_5)_2$.

20 [0057]

Examples of the organoaluminum compounds (B-1b) include $LiAl(C_2H_5)_4$ and $LiAl(C_7H_{15})_4$.

[0058]

Further, other compounds such as methyllithium,

ethylolithium, propyllithium, butyllithium, methylmagnesium bromide, methylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium chloride, propylmagnesium bromide, propylmagnesium chloride, butylmagnesium bromide,
5 butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium and butylethylmagnesium are also employable as the organometallic compounds (B-1).

[0059]

Furthermore, combinations of compounds capable of
10 producing the above-mentioned organoaluminum compounds in the polymerization system, e.g., a combination of halogenated aluminum and alkyllithium and a combination of halogenated aluminum and alkylmagnesium, are also employable.

[0060]

15 Of the organometallic compounds (B-1), the organoaluminum compounds are preferable.

The organometallic compounds (B-1) mentioned above can be used singly or in combination of two or more kinds.

[0061]

20 (B-2) Organoaluminum oxy-compound

The organoaluminum oxy-compound (B-2) for use in the invention may be conventional aluminoxane or a benzene-insoluble organoaluminum oxy-compound exemplified in Japanese Patent Laid-Open Publication No. 78687/1990.

[0062]

The conventional aluminoxane can be prepared by, for example, the following processes, and is generally obtained as a hydrocarbon solvent solution.

5 (1) An organoaluminum compound such as trialkylaluminum is added to a hydrocarbon medium suspension of a compound containing adsorbed water or a salt containing water of crystallization, e.g., magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate, to allow the 10 organoaluminum compound to react with the adsorbed water or the water of crystallization.

(2) Water, ice or water vapor is allowed to directly act on an organoaluminum compound such as trialkylaluminum in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

15 (3) An organotin oxide such as dimethyltin oxide or dibutyltin oxide is allowed to react with an organoaluminum compound such as trialkylaluminum in a medium such as decane, benzene or toluene.

20 [0063]

The aluminoxane may contain a small amount of an organometallic component. Further, it is possible that the solvent or the unreacted organoaluminum compound is distilled off from the recovered solution of aluminoxane and the

remainder is redissolved in a solvent or suspended in a poor solvent for aluminoxane.

[0064]

Examples of the organoaluminum compounds used for preparing the aluminoxane include the same organoaluminum compounds as described for the organoaluminum compound (B-1a).

[0065]

Of these, preferable are trialkylaluminums and tricycloalkylaluminums. Particularly preferable is trimethylaluminum.

The organoaluminum compounds can be used singly or in combination of two or more kinds.

[0066]

Examples of the solvents used for preparing the aluminoxane include hydrocarbon solvents, e.g., aromatic hydrocarbons, such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons, such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions, such as gasoline, kerosine and gas oil; and halides of these aromatic, aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. Also employable are ethers such as ethyl ether and tetrahydrofuran. Of the solvents, particularly

preferable are aromatic hydrocarbons and aliphatic hydrocarbons.

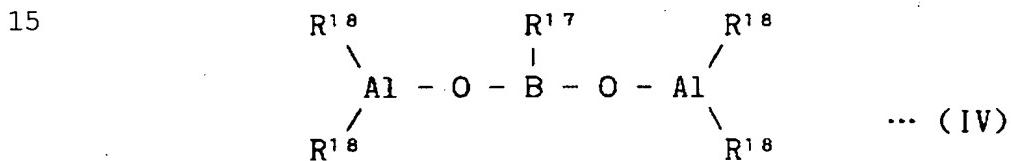
[0067]

In the benzene-insoluble organoaluminum oxy-compound for use in the invention, the content of Al component which 5 is soluble in benzene at 60 °C is usually not more than 10 %, preferably not more than 5 %, particularly preferably not more than 2 %, in terms of Al atom, and the benzene-insoluble organoaluminum oxy-compound is insoluble or sparingly soluble in benzene.

10 [0068]

The organoaluminum oxy-compound used in the invention may include an organoaluminum oxy-compound containing boron and represented by the following formula (IV):

[0069]



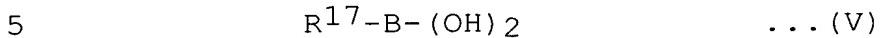
[0070]

wherein R¹⁷ is a hydrocarbon group of 1 to 10 carbon atoms; 20 and each R¹⁸ may be the same or different and is a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 10 carbon atoms.

[0071]

The organoaluminum compound containing boron and represented by the formula (IV) can be prepared by allowing

an alkylboronic acid represented by the following formula (V) to react with an organoaluminum compound in an inert solvent under an inert gas atmosphere at a temperature of -80 °C to room temperature for 1 minute to 24 hours:



wherein R^{17} is the same group as described above.

[0072]

Examples of the alkylboronic acids represented by the formula (V) include methylboronic acid, ethylboronic acid, 10 isopropylboronic acid, n-propylboronic acid, n-butylboronic acid, isobutylboronic acid, n-hexylboronic acid, cyclohexylboronic acid, phenylboronic acid, 3,5-difluoroboronic acid, pentafluorophenylboronic acid and 3,5-bis(trifluoromethyl)phenylboronic acid. Of these, 15 preferable are methylboronic acid, n-butylboronic acid, isobutylboronic acid, 3,5-difluorophenylboronic acid and pentafluorophenylboronic acid. These are used singly or in combination of two or more kinds.

[0073]

20 Examples of the organoaluminum compounds to be reacted with the alkylboronic acid include the same organoaluminum compounds as described for the organoaluminum compound (B-1a).

[0074]

Of these, preferable are trialkylaluminums and

tricycloalkylaluminums. Particularly preferable are trimethylaluminum, triethylaluminum and triisobutylaluminum. The organoaluminum compounds can be used singly or in combination of two or more kinds.

5 [0075]

The organoaluminum oxy-compounds (B-2) mentioned above are used singly or in combination of two or more kinds.

(B-3) Compound which reacts with the transition metal compound to form ion pair

10 The compound (B-3) which reacts with the transition metal compound to form an ion pair (referred to as "ionizing ionic compound" hereinafter), that is used in the invention, is a compound which reacts with the transition metal compound (A) to form an ion pair, and includes Lewis acid, an ionic compound, 15 a borane compound and a carborane compound described in Japanese Patent Laid-Open Publications No. 501950/1989, No. 502036/1989, No. 179005/1991, No. 179006/1991, No. 207703/1991 and No. 207704/1991, and U.S. Patent No. 5,321,106.

[0076]

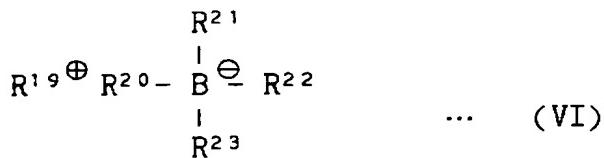
20 The Lewis acid is, for example, a compound represented by BR₃ (R is a phenyl group which may have a substituent such as fluorine, methyl or trifluoromethyl, or a fluorine atom). Examples of such compounds include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron,

tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron.

[0077]

The ionic compound is, for example, a compound
5 represented by the following formula (VI).

[0078]



10 [0079]

In the above formula, R^{19} is H^+ , carbonium cation, oxonium cation, ammonium cation, phosphonium cation, cycloheptyltriaryl cation, ferrocenium cation having a transition metal, or the like.

15 [0080]

R^{20} to R^{23} may be the same or different, and are each an organic group, preferably an aryl group or a substituted aryl group.

Examples of the carbonium cations include

20 tri-substituted carbonium cations, such as triphenylcarbonium cation, tri(methylphenyl)carbonium cation and tri(dimethylphenyl)carbonium cation.

[0081]

Examples of the ammonium cations include

trialkylammonium cations, such as trimethylammonium cation, triethylammonium cation, tripropylammonium cation, tributylammonium cation and tri(n-butyl)ammonium cation; N,N-dialkylanilinium cations, such as N,N-dimethylanilinium cation, 5 N,N-diethylanilinium cation and N,N-2,4,6-pentamethylanilinium cation; and dialkylammonium cations, such as di(isopropyl)ammonium cation and dicyclohexylammonium cation.

[0082]

Examples of the phosphonium cations include

10 triarylphosphonium cations, such as triphenylphosphonium cation, tri(methylphenyl)phosphonium cation and tri(dimethylphenyl)phosphonium cation.

[0083]

R¹⁹ is preferably carbonium cation or ammonium cation, 15 particularly preferably triphenylcarbonium cation, N,N-dimethylanilinium cation or N,N-diethylanilinium cation.

[0084]

Also available as the ionic compound is a trialkyl-substituted ammonium salt, a N,N-dialkylanilinium salt, a 20 dialkylammonium salt and a triarylphosphonium salt.

[0085]

Examples of the trialkyl-substituted ammonium salts include triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron,

tri(n-butyl)ammoniumtetra(phenyl)boron,
trimethylammoniumtetra(p-tolyl)boron,
trimethylammoniumtetra(o-tolyl)boron,
tri(n-butyl)ammoniumtetra(pentafluorophenyl)boron,
5 tripropylammoniumtetra(o,p-dimethylphenyl)boron,
tri(n-butyl)ammoniumtetra(m,m-dimethylphenyl)boron,
tri(n-butyl)ammoniumtetra(p-trifluoromethylphenyl)boron,
tri(n-butyl)ammoniumtetra(3,5-ditrifluoromethylphenyl)boron
and tri(n-butyl)ammoniumtetra(o-tolyl)boron.

10 [0086]

Examples of the N,N-dialkylanilinium salts include
N,N-dimethylaniliniumtetra(phenyl)boron,
N,N-diethylaniliniumtetra(phenyl)boron and
N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

15 [0087]

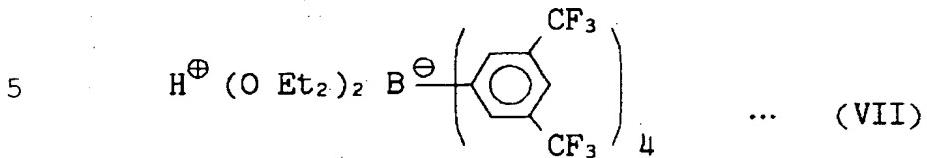
Examples of the dialkylammonium salts include
di(1-propyl)ammoniumtetra(pentafluorophenyl)boron and
dicyclohexylammoniumtetra(phenyl)boron.

[0088]

20 Further employable as the ionic compound is
triphenylcarbeniumtetrakis(pentafluorophenyl)borate,
N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate,
ferroceniumtetra(pentafluorophenyl)borate,
triphenylcarbeniumpentaphenylcyclopentadienyl complex,

N,N-diethylaniliniumpentaphenylcyclopentadienyl complex or a boron compound represented by the following formula (VII) or (VIII).

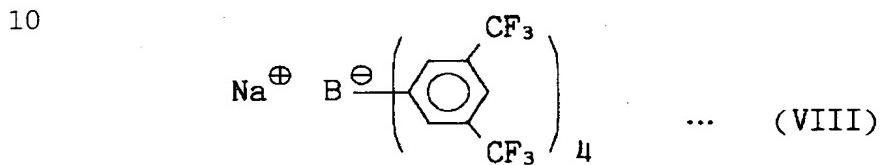
[0089]



[0090]

In the above formula, Et is an ethyl group.

[0091]



[0092]

Examples of the borane compounds include:

15 decaborane(14); salts of anions, such as

bis[tri(n-butyl)ammonium]nonaborate,

bis[tri(n-butyl)ammonium]decaborate,

bis[tri(n-butyl)ammonium]undecaborate,

bis[tri(n-butyl)ammonium]dodecaborate,

20 bis[tri(n-butyl)ammonium]decachlorodecaborate and

bis[tri(n-butyl)ammonium]dodecachlorododecaborate; and

salts of metallic borane anions, such as

tri(n-butyl)ammoniumbis(dodecahydridedodecaborate)cobaltate(III)

and bis[tri(n-butyl)ammonium]bis(dodecahydridedodecaborate)

nickelate(III).

[0093]

Examples of the carborane compounds include:

salts of anions, such as 4-carbanonaborane(14),

- 5 1,3-dicarbanonaborane(13), 6,9-dicarbadeborane(14),
dodecahydride-1-phenyl-1,3-dicarbanonaborane,
dodecahydride-1-methyl-1,3-dicarbanonaborane,
undecahydride-1,3-dimethyl-1,3-dicarbanonaborane,
7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13),
10 undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane,
dodecahydride-11-methyl-2,7-dicarbaundecaborane,
tri(n-butyl) ammonium-1-carbadecaborate,
tri(n-butyl) ammonium-1-carbaundecaborate,
tri(n-butyl) ammonium-1-carbadodecaborate,
15 tri(n-butyl) ammonium-1-trimethylsilyl-1-carbadecaborate,
tri(n-butyl) ammoniumbromo-1-carbadodecaborate,
tri(n-butyl) ammonium-6-carbadecaborate(14),
tri(n-butyl) ammonium-6-carbadecaborate(12),
tri(n-butyl) ammonium-7-carbaundecaborate(13),
20 tri(n-butyl) ammonium-7,8-dicarbaundecaborate(12),
tri(n-butyl) ammonium-2,9-dicarbaundecaborate(12),
tri(n-butyl) ammoniumdodecahydride-8-methyl-7,9-dicarbaundecaborate,
tri(n-butyl) ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate,
tri(n-butyl) ammoniumundecahydride-8-butyl-7,9-dicarbaundecaborate,

tri(n-butyl)ammoniumundecahydride-8-allyl-7,9-dicarbaundecaborate,
tri(n-butyl)ammoniumundecahydride-9-trimethylsilyl-7,8-
dicarbaundecaborate and tri(n-butyl)ammoniumundecahydride-
4,6-dibromo-7-carbaundecaborate; and

5 salts of metallic carborane anions, such as

tri(n-butyl)ammoniumbis(nonahydride-1,3-dicarbanonaborate)
cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-
dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis
(undecahydride-7,8-dicarbaundecaborate)cobaltate(III),

10 tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)
nickelate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-
dicarbaundecaborate)cuprate(III), tri(n-butyl)ammoniumbis
(undecahydride-7,8-dicarbaundecaborate)aurate(III),

tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-
dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis
(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)chromate
(III), tri(n-butyl)ammoniumbis(tribromoóctahydride-7,8-
dicarbaundecaborate)cobaltate(III),

tris[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)

20 chromate(III), bis[tri(n-butyl)ammonium]bis(undecahydride-
7-carbaundecaborate)manganate(IV),

bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)
cobaltate(III) and bis[tri(n-butyl)ammonium]bis(undecahydride-
7-carbaundecaborate)nickelate(IV).

[0094]

The ionizing ionic compounds (B-3) mentioned above can be used singly or in combination of two or more kinds.

In the olefin polymerization catalyst of the invention,
5 the below-described fine particle carrier (C) can be used if necessary, in addition to the above-mentioned transition metal compound (A) and at least one compound (B) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionized ionic compound (B-3).

10 [0095]

(C) Fine particle carrier

The fine particle carrier (C) for use in the invention is an inorganic or organic compound in the form of granular or fine particle solid having a particle diameter of 10 to 300 µm, preferably 20 to 200 µm. As the inorganic compound, porous oxide is preferable. Examples of the porous oxides include SiO₂, Al₂O₃, MgO, ZrO, TiO₂, B₂O₃, CaO, ZnO, BaO, ThO₂; and mixtures containing these oxides, such as SiO₂-MgO, SiO₂-Al₂O₃, SiO₂-TiO₂, SiO₂-V₂O₅, SiO₂-Cr₂O₃ and SiO₂-TiO₂-MgO. Of these,
15 preferable are compounds containing at least one selected from the group of SiO₂ and Al₂O₃ as the main component.

20 [0096]

The inorganic oxides may contain a small amount of carbonate, sulfate, nitrate or oxide component, such as Na₂CO₃,

K₂CO₃, CaCO₃, MgCO₃, Na₂SO₄, Al₂(SO₄)₃, BaSO₄, KNO₃, Mg(NO₃)₂, Al(NO₃)₃, Na₂O, K₂O or Li₂O.

[0097]

Though the fine particle carrier (C) differ in their properties depending on the type and the preparation process thereof, the carrier preferably used in the invention has a specific surface area of 50 to 1,000 m²/g, preferably 100 to 700 m²/g, and a pore volume of 0.3 to 2.5 cm³/g. The carrier can be used after calcined at 100 to 1,000 °C, preferably 150 to 700 °C, if desired.

[0098]

The fine particle carrier (C) is, for example, a granular or particle solid of organic compound having a particle diameter of 10 to 300 µm. Examples of such organic compounds include (co)polymers produced using, as main components, α-olefins of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, and (co)polymers produced using, as a main component, vinylcyclohexane or styrene.

[0099]

The olefin polymerization catalyst according to the invention comprises the above-mentioned transition metal compound (A) and at least one compound (B) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionized ionic compound (B-3) and

optionally the fine particle carrier (C).

[0100]

In the polymerization, the components can be used in any way and in any order. Some examples of the processes are given below.

5 (1) The component (A) and at least one component (B) selected from the organometallic compound (B-1), the organoaluminum oxy-compound (B-2) and the ionized ionic compound (B-3) (referred to simply as "component (B)" hereinafter) are fed to the polymerization reactor in an arbitrary order.

10 (2) A catalyst previously contacted the component (A) with the component (B) is fed to the polymerization reactor.

(3) A catalyst component previously contacted the component (A) with the component (B), and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, 15 the components (B) may be the same or different.

(4) A catalyst component wherein the component (A) is supported on the fine particle carrier (C), and the component (B) are fed to the polymerization reactor in an arbitrary order.

(5) A catalyst wherein the component (A) and the component 20 (B) are supported on the fine particle carrier (C) is fed to the polymerization reactor.

(6) A catalyst component wherein the component (A) and the component (B) are supported on the fine particle carrier (C), and the component (B) are fed to the polymerization reactor

in an arbitrary order. In this case, the components (B) may be the same or different.

(7) A catalyst component wherein the component (B) is supported on the fine particle carrier (C), and the component 5 (A) are fed to the polymerization reactor in an arbitrary order.

(8) A catalyst component wherein the component (B) is supported on the fine particle carrier (C), the component (A) and the component (B) are fed to the polymerization reactor in an arbitrary order. In this case, the components (B) may

10 be the same or different.

[0101]

For the solid catalyst component wherein the component (A) and the component (B) are supported on the fine particle carrier (C), an olefin may be prepolymerized.

15 In the process for olefin polymerization according to the invention, an olefin is polymerized or copolymerized in the presence of the above-described olefin polymerization catalyst to obtain an olefin polymer.

[0102]

20 In the present invention, the polymerization can be carried out as any of liquid phase polymerization, such as solution polymerization or suspension polymerization, and gas phase polymerization.

Examples of the inert hydrocarbon media used in the

liquid phase polymerization include aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosine; alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane; aromatic hydrocarbons, such as benzene, toluene and xylene; halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons. The olefin itself can be used as the solvent.

[0103]

In the polymerization of an olefin using the olefin polymerization catalyst, the component (A) is used in an amount of usually 10^{-8} to 10^{-2} mol, preferably 10^{-7} to 10^{-3} mol, based on 1 liter of the reaction volume.

[0104]

The component (B-1) is used in such an amount that the molar ratio of the component (B-1) to the transition metal atom (M) in the component (A) ($(B-1)/(M)$) becomes usually 0.01 to 5,000, preferably 0.05 to 2,000. The component (B-2) is used in such an amount that the molar ratio of the aluminum atom in the component (B-2) to the transition metal atom (M) in the component (A) ($((B-2)/(M))$) becomes usually 10 to 5,000, preferably 20 to 2,000. The component (B-3) is used in such an amount that the molar ratio of the component (B-3) to the transition metal atom (M) in the component (A) ($((B-3)/(M))$)

becomes usually 1 to 10, preferably 1 to 5.

[0105]

The temperature for the olefin polymerization using the olefin polymerization catalyst is in the range of usually -50 to 5 200 °C, preferably 0 to 170 °C. The polymerization pressure is in the range of usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The polymerization reaction can be carried out by any of batchwise, semi-continuous and continuous processes. The polymerization can be conducted 10 in two or more stages under different reaction conditions.

[0106]

The molecular weight of the resulting polymer can be adjusted by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature.

15 Further, the molecular weight can be adjusted also by using the component (B) of different type.

[0107]

Examples of the olefins which can be polymerized using the olefin polymerization catalyst include:

20 α-olefins of 2 to 30, such as ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and cycloolefins of 3 to 20, such as cyclopentene,

cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8a-octahydronaphthalene.

polar monomers, such as α,β -unsaturated carboxylic acids,

- 5 e.g., acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, itaconic anhydride and bicyclo(2,2,1)-5-heptene-2,3-dicarboxylic acid, and metallic salts of these acids, e.g., sodium salts, potassium salts, lithium salts, zinc salts, magnesium salts and calcium salts;
- 10 α,β -unsaturated carboxylic esters, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate and isobutyl methacrylate; vinyl esters, such as 15 vinyl acetate, vinyl propionate, vinyl caproate, vinyl caprate, vinyl laurate, vinyl stearate and vinyl trifluoroacetate; and unsaturated glycidyl esters, such as glycidyl acrylate, glycidyl methacrylate and monoglycidyl itaconate. Furthermore, 20 styrene, vinylcyclohexane, diene and the like are also employable.

[0108]

[Effect of the invention]

The olefin polymerization catalyst according to the invention has high polymerization activities on olefins and

provides a polymer having a narrow molecular weight distribution. When two or more kinds of olefins are copolymerized, an olefin copolymer having a narrow composition distribution can be obtained.

5 [0109]

In the process for olefin polymerization according to the invention, a polymer having a narrow molecular distribution can be produced with high polymerization activities. When two or more kinds of olefins are copolymerized, an olefin copolymer 10 having a narrow composition distribution can be prepared.

[0110]

[Example]

The present invention is further described with reference to the following examples, but it should be construed 15 that the invention is in no way limited to those examples.

[0111]

Further, the intrinsic viscosity [η] was measured in decalin at 135 °C and represented by dl/g.

[0112]

20 [Synthesis Example 1]

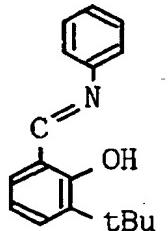
Synthesis of compound (A-1)

To a 100 ml reactor thoroughly purged with nitrogen, 40 ml of ethanol, 0.71 g (7.62 mmol) of aniline and 1.35 g (7.58 mmol) of 3-t-butylsalicylaldehyde were introduced, and they

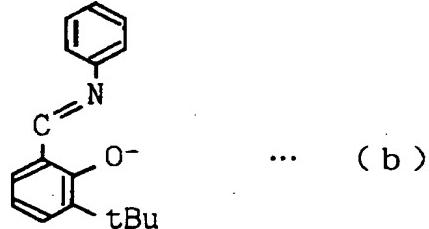
were stirred at room temperature for 24 hours. The reaction solution was concentrated under reduced pressure to remove the solvent. Then, 40 ml of ethanol was added again, and the mixture was stirred at room temperature for 12 hours. The 5 reaction solution was concentrated under reduced pressure to obtain 1.83 g (yield: 95 %) of a compound represented by the following formula (a) as an orange oil. The energy difference between HOMO and LUMO in a state of anionizing this compound (following formula (b)) calculated by the Hamiltonian PM3 10 method of MOPAC VERSION 6.00 was 6.38 eV.

[0113]

15



... (a)



... (b)

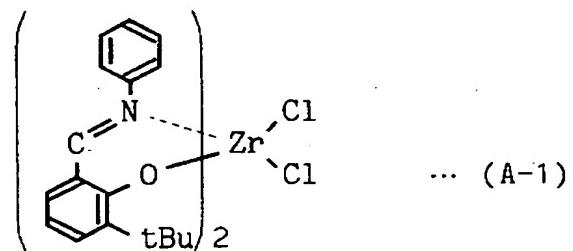
[0114]

To a 200 ml reactor thoroughly purged with nitrogen, 0.50 g (1.97 mmol) of compound (a) obtained above and 50 ml of absolute 20 diethyl ether were introduced, and they were cooled to -78 °C and stirred. After 1.28 ml of n-butyllithium (1.63N n-hexane solution, 2.09 mmol) was dropped over a period of 5 minutes, the temperature was slowly raised to room temperature. The solution was stirred for 4 hours at room temperature, and then

was cooled to -78 °C again. After 0.37g (0.98 mmol) of ZrCl₄ · THF₂ was slowly added, the reaction solution was slowly raised to room temperature. After the solution was stirred for 2 hours at room temperature, 50 mL of absolute tetrahydrofuran 5 was added, and the mixture was stirred for 3 hours under reflux. The reaction solution was concentrated under reduced pressure, and the solid precipitated was washed with 100 mL of absolute diethyl ether. The resulting solid was washed with 100 ml of absolute methylene chloride to remove insolubles. The 10 resulting methylene chloride solution was concentrated under reduced pressure, and the solid precipitated was washed with 50 ml of mixture of absolute diethyl ether and absolute hexane (absolute diethyl ether : absolute hexane = 1:1). The resulting solid was dried under reduced pressure to obtain 0.38 15 g (yield: 58 %) of compound (A-1) represented by the following formula as brownish green crystals. The result of FD-mass spectrometry of compound (A-1) is 664(M⁺).

[0115]

20



... (A-1)

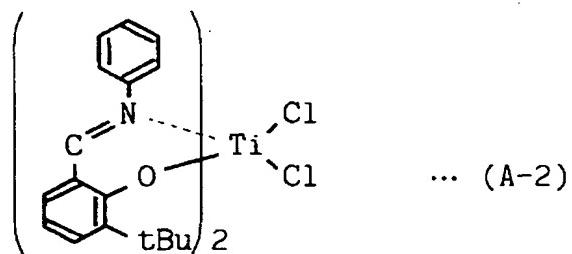
[0116]

[Synthesis Example 2]

Synthesis of compound (A-2)

To a 200 ml reactor thoroughly purged with nitrogen, 0.60 g (2.37 mmol) of compound (a) and 50 ml of absolute diethyl ether were introduced, and they were cooled to -78 °C and stirred. After 1.53 ml of n-butyllithium (1.63N n-hexane solution, 2.49 mmol) was dropped over a period of 5 minutes, the temperature was slowly raised to room temperature. The solution was stirred for 4 hours at room temperature, and then 10 was cooled to -40 °C again. After 2.4 mL (0.5 mmol/ml decane solution, 1.20 mmol) of TiCl₄ was slowly added, the reaction solution was slowly raised to room temperature. After the solution was stirred for 4 hours at room temperature, the solution was filtered with a glass filter and the solid 15 precipitated was washed with 100 ml of absolute diethyl ether. The resulting solid was washed with 100 ml of absolute methylene chloride to remove insolubles. The resulting methylene chloride solution was concentrated under reduced pressure, and the solid precipitated was washed with 100 ml of absolute hexane. 20 The deposited solid was dried under reduced pressure to obtain 0.20 g (yield: 27 %) of compound (A-2) represented by the following formula as orange crystals. The result of FD-mass spectrometry of compound (A-2) is 622(M⁺).

[0117]



5

[0118]

[Example 1]

Polymerization

To a 500 ml glass autoclave thoroughly purged with
 10 nitrogen, 250 ml of toluene was introduced, and the liquid phase
 and the gas phase were saturated with ethylene. Thereafter,
 1.1875 mmol (in terms of aluminum atom) of methylaluminoxane
 was added, and successively 0.00475 mmol of the zirconium
 compound (A-1) obtained in the Synthesis Example 1 was added
 15 to initiate polymerization. The reaction was conducted at
 25 °C for 30 minutes in an ethylene gas atmosphere at normal
 pressure, and then a small amount of isobutanol was added to
 terminate the polymerization. After the polymerization was
 completed, the reaction product was introduced into a large
 20 amount of methanol to precipitate a polymer in the whole amount.
 Then, hydrochloric acid was added, and filtration was effected
 using a glass filter. The resulting polymer was vacuum dried
 at 80 °C for 10 hours to obtain 24.67 g of polyethylene (PE).

[0119]

The polymerization activity per 1 mmol of zirconium was 10,400 g, and the intrinsic viscosity [η] of the polyethylene was 0.91 dl/g.

[0120]

5 [Example 2]

Polymerization

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 10 0.25 mmol of triisobutylaluminum was added, and successively 0.0025 mmol of the zirconium compound (A-1) obtained in the Synthesis Example 1 and 0.005 mmol of triphenylcarbeniumtetrakis (pentafluorophenyl)borate were added to initiate polymerization. The reaction was conducted at 25 °C for 3 minutes in an ethylene 15 gas atmosphere at normal pressure. After the polymerization was completed, the reaction product was introduced into a large amount of methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried 20 at 80 °C for 10 hours to obtain 2.36 g of polyethylene (PE).

[0121]

The polymerization activity per 1 mmol of zirconium was 18,900 g, and the intrinsic viscosity [η] of the polyethylene was 1.56 dl/g.

[0122]

[Example 3]

Polymerization

To a 500 ml glass autoclave thoroughly purged with nitrogen,

5 250 ml of toluene was introduced, and the liquid phase and the
gas phase were saturated with ethylene. Thereafter, 1.1875
mmol of methylaluminoxane in terms of aluminum atom was added,
and successively 0.00475 mmol of the titanium compound (A-2)
obtained in the Synthesis Example 2 was added to initiate
10 polymerization. The reaction was conducted at 25 °C for 30
minutes in an ethylene gas atmosphere at normal pressure.
After the polymerization was completed, the reaction product
was introduced into a large amount of methanol to precipitate
a polymer in the whole amount. Then, hydrochloric acid was
15 added, and filtration was effected using a glass filter. The
resulting polymer was vacuum dried at 80 °C for 10 hours to
obtain 8.02 g of polyethylene (PE).

[0123]

The polymerization activity per 1 mmol of titanium was
20 3,400 g, and the intrinsic viscosity [η] of the polyethylene
was 8.44 dl/g.

[0124]

[Example 4]

Polymerization

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 0.11875 mmol of methylaluminoxane in terms of aluminum atom was added, 5 and successively 0.000475 mmol of the compound (A-2) obtained above was added to initiate polymerization. The reaction was conducted at 25 °C for 1 hour in an ethylene gas atmosphere at normal pressure. After the polymerization was completed, the reaction product was introduced into a large amount of 10 methanol to precipitate a polymer in the whole amount. Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried at 80 °C for 10 hours to obtain 0.50 g of polyethylene (PE).

[0125]

15 The polymerization activity per 1 mmol of titanium was 100 g, and the intrinsic viscosity [η] of the polyethylene was 106 dl/g.

[0126]

[Example 5]

20 Polymerization

To a 500 ml glass autoclave thoroughly purged with nitrogen, 250 ml of toluene was introduced, and the liquid phase and the gas phase were saturated with ethylene. Thereafter, 0.25 mmol of triisobutylaluminum was added, and successively 0.005 mmol

of the titanium compound (A-2) obtained in the Synthesis Example 2 and 0.006 mmol of triphenylcarbeniumtetrakis (pentafluorophenyl)borate were added to initiate polymerization.

The reaction was conducted at 25 °C for 1 hour in an ethylene

5 gas atmosphere at normal pressure. After the polymerization was completed, the reaction product was introduced into a large amount of methanol to precipitate a polymer in the whole amount.

Then, hydrochloric acid was added, and filtration was effected using a glass filter. The resulting polymer was vacuum dried

10 at 80 °C for 10 hours, to obtain 0.50 g of polyethylene.

[0127]

The polymerization activity per 1 mmol of titanium was 100 g, and the intrinsic viscosity [η] of the polyethylene was 10.6 dl/g.

15 [Brief description of the drawings]

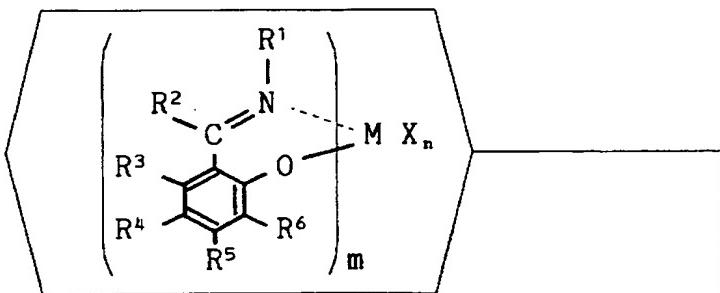
Fig. 1 shows steps for preparing the olefin polymerization catalyst according to the invention.

[Document] Drawing

[Fig.1]

(A) Transition metal component

5



M: transition metal atom of group 3-11 of the periodic table

10 R¹-R⁶: hydrogen, hydrocarbon group, etc.

m: 1-3 n: 1-3

X: halogen, hydrocarbon group, etc.

(B) Organometal component

15

Organometallic compound

Olefin

Organoaluminum oxy-compound

Compound reacting with transition
metal compound to form ion pair

20

(C) Third component

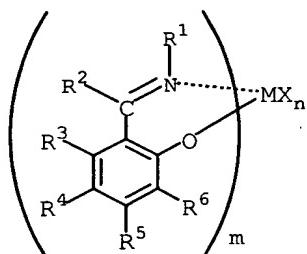
(Fine particle carrier)

[Document] Abstract

[Summary]

The present invention relates to provide an olefin polymerization catalyst having excellent olefin polymerization activities and a process for preparation of the polymerization an olefin using the catalyst.

The olefin polymerization catalyst comprises (A) a transition metal compound represented by the following formula (I), and (B) an organometallic compound, an organoaluminum oxy-compound or an ionizing ionic compound.



M: transition metal of group 3-11 of the periodic table
 $R^1 - R^6$: hydrogen atom, hydrocarbon group, etc.
 $\dots (I)$ m: 1-3 n: 1-3
X: halogen atom, hydrocarbon group, etc.

15

[Selected figure] Fig.1

20